REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
24-03-2018	Final Report	19-Jun-2014 - 22-Dec-2017

4. TITLE AND SUBTITLE
Final Report: Highly Conductive Anion Exchange Block Copolymers

5a. CONTRACT NUMBER
W911NF-14-1-0310

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Texas Engineering Experiment Station
SRS
400 Harvey Mitchell Parkway South, Suite 300
College Station, TX 77845 -4375

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
63204-CH.15

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Yossef Elabd
UU	UU	UU	UU		19b. TELEPHONE NUMBER
					979-845-7506

RPPR Final Report
as of 19-Apr-2018

Agency Code:

Proposal Number: 63204CH **Agreement Number: W911NF-14-1-0310**
INVESTIGATOR(S):

Name: Yossef A. Elabd elabd@drex
Email: elabd@tamu.edu
Phone Number: 9798457506
Principal: Y

Organization: **Texas Engineering Experiment Station**
Address: SRS, College Station, TX 778454375
Country: USA
DUNS Number: 847205572 EIN: 741974733
Report Date: 22-Mar-2018 Date Received: 24-Mar-2018
Final Report for Period Beginning 19-Jun-2014 and Ending 22-Dec-2017
Title: Highly Conductive Anion Exchange Block Copolymers
Begin Performance Period: 19-Jun-2014 **End Performance Period:** 22-Dec-2017
Report Term: 0-Other
Submitted By: Yossef Elabd Email: elabd@tamu.edu
Phone: (979) 845-7506
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 4 **STEM Participants:** 5

Major Goals: We are developing a comprehensive fundamental understanding of the interplay between transport and morphology in newly synthesized hydroxide conducting block copolymers. We are synthesizing hydroxide conducting block copolymers of various (1) morphology types, (2) ionic concentrations, and (3) ionic domain sizes. We are carefully characterizing the morphology and transport properties using both conventional and new advanced in situ techniques that have recently been developed in our laboratory. This exploration into hydroxide conducting block copolymers is an unexplored area of research, where the outcomes of this research will provide a new body of knowledge in the field of polymer science and a fundamental understanding of transport-morphology relationships in hydroxide conducting block copolymers for the development of robust highly hydroxide conductive polymers that will result in high power density, long-lasting, low-cost alkaline fuel cells.

Accomplishments: Please see PDF document uploaded in "Upload" section.

RPPR Final Report
as of 19-Apr-2018

Training Opportunities: Training Opportunities:

Students trained include:

Rishon Benjamin - received his B.S. from Drexel University, June 2015. He is currently a graduate student at M.I.T.

Kelly M. Meek - received her Ph.D. from Texas A&M University, May 2016. She is currently postdoc at Oak Ridge National Laboratory (ORNL). She will be seeking future faculty position.

Dissertation: Meek, K.M. Ph.D. Dissertation, Alkaline Chemical Stability and Ion Transport in Polymerized Ionic Liquid Anion Exchange Membranes, Texas A&M University, May 2016.

Jacob R. Nykaza - received his Ph.D. from Drexel University, April 2016. He is currently employed at Teledyne Technologies

Dissertation: Nykaza, J.R. Ph.D. Dissertation, Imidazolium-Based Block Copolymers as Solid-State Separators for Alkaline Fuel Cells and Lithium Ion Batteries, Drexel University, April 2016.

Rui Sun - received her M.S. from Texas A&M University, August 2016. She is now a Ph.D. student at Texas A&M University and working on this project.

Thesis: Sun, R. M.S. Thesis, Polymerized Ionic Liquid Derived Carbon, Texas A&M University, August 2016.

Patrick Lathrop - is currently a Ph.D. student at Texas A&M University and is working on this project.

RPPR Final Report
as of 19-Apr-2018

Results Dissemination: Results Dissemination:

Key Peer-Reviewed Publications:

1. Meek, K.M.; Sun, R.; Willis, C.; Elabd, Y.A. Hydroxide Conducting Polymerized Ionic Liquid Pentablock Terpolymer Anion Exchange Membranes with Methylpyrrolidinium Cations. Polymer 2018, 134, 221-226.

2. Nykaza, J.R.; Li, Y.; Elabd, Y.A.; Snyder, J.D. Effect of Alkaline Exchange Polymerized Block Copolymer Ionomers on the Kinetics of Fuel Cell Half Reactions. J. Electroanalytical Chem. 2016, 783, 182-187.

3. Nykaza, J.R.; Savage, A.M.; Pan, Q.; Wang, S.; Beyer, F.L.; Tang, M.H.; Li, C.Y.; Elabd, Y.A. Polymerized Ionic Liquid Diblock Copolymer as Solid-State Separator and Electrolyte in Lithium-Ion Battery. Polymer 2016, 101, 311-318.

4. Nykaza, J.R.; Benjamin, R.; Meek, K.M. Elabd, Y.A. Polymerized Ionic Liquid Diblock Copolymer as an Ionomer and Anion Exchange Membrane for Alkaline Fuel Cells. Chemical Engineering Science 2016, 154, 119-127. Invited Contribution, Special Issue on Recent Advances in Energy Conversion and Storage Devices

5. Meek, K.M.; Elabd, Y.A. Sulfonated Polymerized Ionic Liquid Block Copolymers. Macromolecular Rapid Comm. 2016, 37, 1200-1206. Invited Contribution, Special Issue on Ionic Liquids in Polymer Design

6. Meek, K.M.; Nykaza, J.R.; Elabd, Y.A. Alkaline Chemical Stability and Ion Transport in Polymerized Ionic Liquids with Various Backbones and Cations. Macromolecules 2016, 49, 3382-2294.

7. Nykaza, J.R.; Ye, Y.; Nelson, R.L.; Jackson, A.C.; Beyer, F.L.; Davis, E.M.; Page, K.A. Sharick, S.; Winey, K.I.; Elabd, Y.A. Polymerized Ionic Liquid Diblock Copolymers: Impact of Water/Ion Clustering on Ion Conductivity. Soft Matter 2016, 12, 1133-1144.

8. Meek, K.M.; Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers for Electrochemical Energy. Journal of Materials Chemistry A 2015, 3, 24187-24194. Invited Contribution

9. Meek, K.M.; Elabd, Y.A. Alkaline Chemical Stability of Polymerized Ionic Liquids with Different Cations. Macromolecules 2015, 48, 7071-7084.

10. Ansaloni, L.; Nykaza, J.R.; Ye, Y.; Elabd, Y.A.; Giacinti Baschetti, M. Influence of Water Vapor on the Gas Permeability of Polymerized Ionic Liquid Membranes. J. Membr. Sci., 2015, 487, 199-208.

11. Meek, K.M.; Sharick, S.; Ye, Y.; Winey, K.I.; Elabd, Y.A. Bromide and Hydroxide Conductivity-Morphology Relationships in Polymerized Ionic Liquid Block Copolymers. Macromolecules 2015, 48, 4850-4862.

12. Nykaza, J.R.; Ye, Y.; Elabd, Y.A. Polymerized Ionic Liquid Diblock Copolymers with Long Alkyl Side-Chain Length. Polymer 2014, 55, 3360-3369. Invited Contribution, Special Issue on Polymerized Ionic Liquids

Key Presentations:

Oral Presentations:

1. Sun, R.; Meek, K.M.; Elabd, Y.A. Carbon Derived from Polymerized Ionic Liquids. AIChE Annual Meeting, Minneapolis, MN, November 2017.

2. Meek, K.M.; Nykaza, J., Sun, R.; Willis, C.L.; Elabd, Y.A. Chemical Stability and Ion Transport in Polymerized Ionic Liquid Anion Exchange Membranes. Fall National Meeting of the American Chemical Society, Washington, D. C., August 2017. Selected as DSM Science & Technology Award Finalist

3. Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers for Alkaline Fuel Cells. Materials Research Society Fall National Meeting, Boston, MA, November 2016. Invited Speaker

4. Meek, K.M.; Nykaza, J., Sun, R.; Willis, C.L.; Elabd, Y.A. Chemical Stability and Ion Transport in Polymerized

Ionic Liquid Anion Exchange Membranes. AIChE Annual Meeting, San Francisco, CA, November 2016. Selected for Excellence in Graduate Polymer Research Session - Received 2nd Place Award in Session

5. Santos, M.; Elabd, Y.A. In Situ Pressure-Contact Time-Resolved Fourier Transform Infrared Attenuated Total Reflectance Spectroscopy: A New Method to Measure Liquid Diffusion in Free-Standing Polymer Films. AIChE Annual Meeting, San Francisco, CA, November 2016. AIChE, San Francisco, CA, November 2016.

6. Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers for Alkaline Fuel Cells. American Chemical Society Southwest Regional Meeting (ACS-SWRM), Galveston, TX, November 2016. Invited Speaker

7. Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers. American Chemical Society Meeting on Advanced Polymer Materials (ACS-APM), Houston, TX, November 2016. Invited Speaker

8. Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers for Alkaline Fuel Cells. 15th International Symposium on Polymer Electrolytes. Uppsala, Sweden, August 2016. Invited Speaker

9. Elabd, Y.A. Membranes for Fuel Cells. European Membrane Society Summer School, Bertinoro, Italy, June 2016. Invited Speaker

10. Meek, K.M.; Savage, A.M.; Beyer, F.L.; Elabd, Y.A. Chemical Stability and Ion Transport in Polymerized Ionic Liquid Block Copolymer Anion Exchange Membranes with Various Cations. AIChE Annual Meeting, Salt Lake City, UT, November 2015.

11. Nykaza, J.R.; Li, Y.; Elabd, Y.A.; Snyder, J. The Hydroxide Conductivity and Chemical Stability of a Polymerized Ionic Liquid Diblock Copolymer for Alkaline Fuel Cells Using Rotating Disk Electrode. AIChE Annual Meeting, Salt Lake City, UT, November 2015.

12. Elabd, Y.A. Polymerized Ionic Liquid Block Copolymer as Anion Exchange Membranes. Fall National Meeting of the American Chemical Society, Boston, MA, August 2015. Invited Speaker

13. Meek, K.M.; Beyer, F.L.; Elabd, Y.A. Transport and Morphology of Polymerized Ionic Liquid Block Copolymer Anion Exchange Membranes with Various Cations. Spring National Meeting of the American Chemical Society, Denver, CO, March 2015.

14. Nykaza, J.R.; Sharick, S.; Davis, E.M.; Ye, Y.; Page, K.A.; Jackson, A.; Beyer, F.L.; Winey, K.I.; Elabd, Y.A. Impact of Alkyl Chain Length on Ion Conduction and Morphology in Polymerized Ionic Liquid Diblock Copolymers. Spring National Meeting of the American Chemical Society, Denver, CO, March 2015.

15. Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers: Highly Versatile Ion Conductors. Annual Meeting of the American Institute of Chemical Engineers, Atlanta, GA, November 2014. Invited Speaker

16. Ye, Y.; Nykaza, J.R.; Meek, K.M.; Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers as Anion Exchange Membranes for Alkaline Fuel Cells. Annual Meeting of the American Institute of Chemical Engineers, Atlanta, GA, November 2014. Invited Speaker

17. Ansaloni, L.; Nykaza, J.R.; Minelli, M.; Elabd, Y.A.; Giaciniti Baschetti, M. Polymerized Ionic Liquid Membranes for CO2 Capture: The Effect of Water Vapor. Annual Meeting of the American Institute of Chemical Engineers, Atlanta, GA, November 2014.

Poster Presentations:

18. Sun, R.; Meek, K.M.; Elabd, Y.A. PIL-Derived Carbon. AIChE Annual Meeting, San Francisco, CA, November 2016.

19. Lathrop, P.; Elabd, Y.A. Polymerized Ionic Liquid Triblock Terpolymers: Synthesis and Characterization. AIChE Annual Meeting, San Francisco, CA, November 2016.

20. Benjamin, R.; Nykaza, J.R.; Elabd, Y.A. Alkaline Fuel Cell Performance with a Polymerized Ionic Liquid Block Copolymer as Anion Exchange Membrane. Annual Meeting of the American Institute of Chemical Engineers,

Atlanta, GA, November 2014. Received 3rd Place Award in the Materials Science and Engineering Poster Competition

21. Nykaza, J.R.; Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers as Solid-State Polymer Electrolytes for Lithium-Ion Batteries. Annual Meeting of the American Institute of Chemical Engineers, Atlanta, GA, November 2014.

Honors and Awards: Honors:

Prof. Elabd was elected as an APS Fellow

Prof. Elabd was named the Joe M. Nesbitt Professor

Kelly Meek received 2017 DSM Science & Technology Award Finalist (@Fall 2017 ACS National Meeting)

Kelly Meek received 2nd Place Award in Excellence in Graduate Polymer Research Session (@2016 AIChE National Meeting)

Kelly Meek received the 2015 Phillips 66 Fellowship (awarded to top PhD student in Chemical Engineering Department at Texas A&M University)

Protocol Activity Status:

Technology Transfer: Technology Transfer:

Collaboration with industry - Kraton Polymers - one co-authored publication.

Meek, K.M.; Sun, R.; Willis, C.; Elabd, Y.A. Hydroxide Conducting Polymerized Ionic Liquid Pentablock Terpolymer Anion Exchange Membranes with Methylpyrrolidinium Cations. Polymer 2018, 134, 221-226.

PARTICIPANTS:

Participant Type: PD/PI
Participant: Yossef A Elabd
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Kelly M Meek
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Jacob R Nykaza
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:

National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Rui Sun
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Patrick Lathrop
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Rishon Benjamin
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

DISSERTATIONS:

Publication Type: Thesis or Dissertation
Institution: Texas A&M University
Date Received: 31-Aug-2016 Completion Date: 5/2/16 12:27AM
Title: ALKALINE CHEMICAL STABILITY AND ION TRANSPORT IN POLYMERIZED IONIC LIQUID ANION EXCHANGE MEMBRANES
Authors: Kelly Meek
Acknowledged Federal Support: **Y**

Publication Type: Thesis or Dissertation
Institution: Drexel University
Date Received: 31-Aug-2016 Completion Date: 4/2/16 12:27AM
Title: Imidazolium-based Block Copolymers as Solid-State Separators for Alkaline Fuel Cells and Lithium Ion Batteries
Authors: Jacob Nykaza
Acknowledged Federal Support: **N**

RPPR Final Report
as of 19-Apr-2018

Publication Type: Thesis or Dissertation
Institution: Texas A&M University
Date Received: 31-Aug-2016 Completion Date: 8/2/16 12:27AM
Title: POLYMERIZED IONIC LIQUID DERIVED CARBON
Authors: Rui Sun
Acknowledged Federal Support: **N**

Final Report
December 22, 2017
Period: 06/19/14-12/22/17
ARO Proposal Number: 63204-CH
Agreement Number: W911NF-14-0310

Highly Conductive Anion Exchange Block Copolymers
PI: Y.A. Elabd

Major Goals:

We are developing a comprehensive fundamental understanding of the interplay between transport and morphology in newly synthesized hydroxide conducting block copolymers. We are synthesizing hydroxide conducting block copolymers of various (1) morphology types, (2) ionic concentrations, and (3) ionic domain sizes. We are carefully characterizing the morphology and transport properties using both conventional and new advanced *in situ* techniques that have recently been developed in our laboratory. This exploration into hydroxide conducting block copolymers is an *unexplored area* of research, where the outcomes of this research will provide a new body of knowledge in the field of polymer science and a fundamental understanding of transport-morphology relationships in hydroxide conducting block copolymers for the development of robust highly hydroxide conductive polymers that will result in high power density, long-lasting, low-cost alkaline fuel cells.

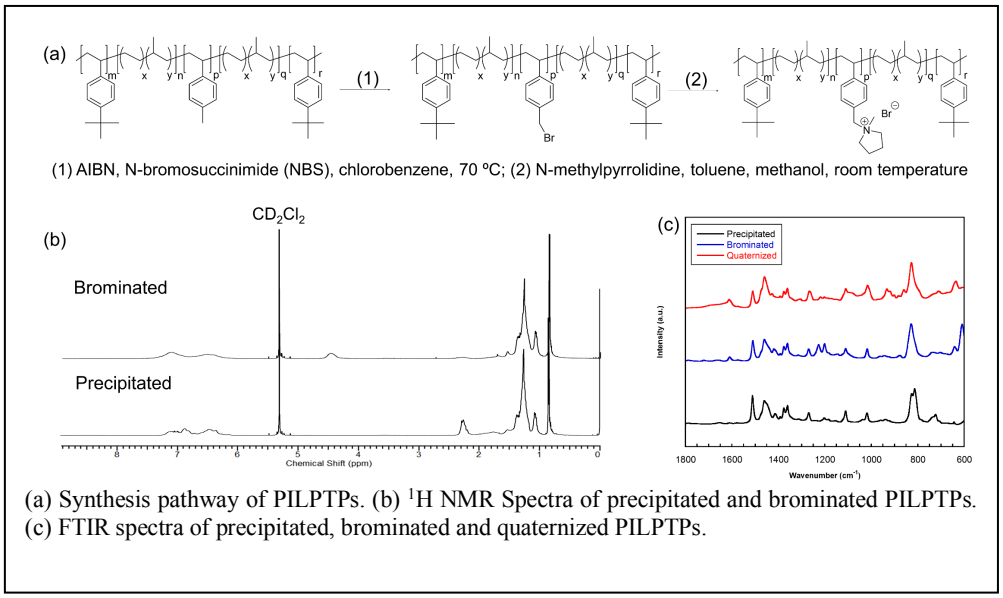
Accomplished:

Key Results:

1. Polymerized Ionic Liquid Pentablock Terpolymer (PILPTP) Synthesis and Application

The synthesis and characterization of commercially available solid-state anion exchange membrane (AEM) is of great interest for the development of alkaline fuel cell (AFC). In this study, a pentablock terpolymer that contains tert-butyl-styrene as the A outer blocks (tert-butyl-styrene: tbS), a random copolymer of ethylene-r-propylene blocks (ethylene-r-propylene: EP) as the B blocks, and pyrrolidinium-functionalized styrene PIL midblock (vinylbenzylmethypyrrolidinium bromide: VBMPyr-Br) as the inner C block (see figure below) was proposed and will be investigated as a promising AEM for the AFC. A commercially available ABCBA pentablock terpolymer from Kraton Performance Polymers, poly(tbS-b-EP-b-pMS-b-EP-b-tbS), was applied as polymer precursor for bromination and functionalization reactions. Bromination reactions were performed by using N-bromosuccinimide (NBS) and azobisisobutyronitrile (AIBN) as reactants with various reactant ratios. The degree of bromination was determined by ^{1}H NMR spectroscopy by calculating the ratio of the benzylic proton to the remaining methyl protons. Subsequently, the brominated polymers were quaternized in toluene/methanol mixture with various reactant ratio and reaction time. The degree of quaternization was qualitatively examined by EA (nitrogen composition) and FTIR-ATR Spectroscopy (disappearance of the benzyl bromide bond vibrational band at 1230 cm^{-1}). Ion exchange capacities (IECs) were determined by the titration of the bromide ions from ion exchange reactions with sodium nitrite. Preliminary results indicate the successful

synthesis of the proposed PILPTP. ^{1}H NMR spectroscopy confirmed that different degree of bromination was achieved. FTIR spectra showed that a small portion of the CH_2-Br vibrational band were still able to be observed after the quaternization. EA indicated that the compositions of the polymers did not vary much with the increase of the methylpyrrolidine amount. Daily experiments suggested that the duration of the functionalization does not make significant difference in the degree of functionalization and the IECs. Future work will be focusing on the investigating the conductivity and morphology of PILPTP under various conditions and its further applications in energy storage devices.

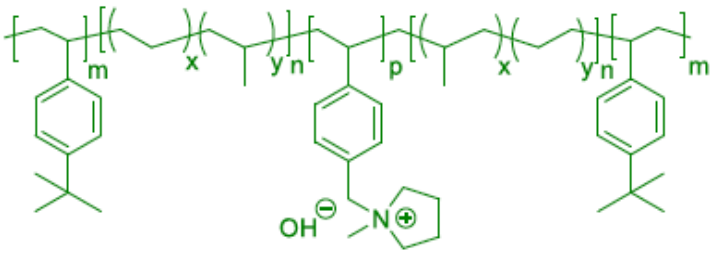


(a) Synthesis pathway of PILPTPs. (b) ^{1}H NMR Spectra of precipitated and brominated PILPTPs. (c) FTIR spectra of precipitated, brominated and quaternized PILPTPs.

2. Hydroxide Conducting Polymerized Ionic Liquid Pentablock Terpolymers with Methylpyrrolidinium Cations as Anion Exchange Membranes

A commercially scalable polymerized ionic liquid (PIL) pentablock terpolymer anion exchange membrane (AEM) from previous results was investigated for use in alkaline fuel cells (AFCs). The transparent, flexible AEMs exhibited hydroxide ion conductivities of 44 mS/cm at 60 °C in liquid water. AEMs demonstrated excellent alkaline chemical stability, with no change in ion conductivity after exposure to 1 M KOH solution at 60 °C for 1 week. Additionally, ^{1}H NMR analysis of the analogous polymerized ionic liquid (PIL) homopolymer revealed no degradation in 0.5 M KOH solution at 60 °C for 1 week. These results indicate that this commercially scalable multiblock polymer is a highly conductive, chemically stable, robust AEM, suitable for use in low-cost (platinum-free), long-lasting, solid-state alkaline fuel cells.

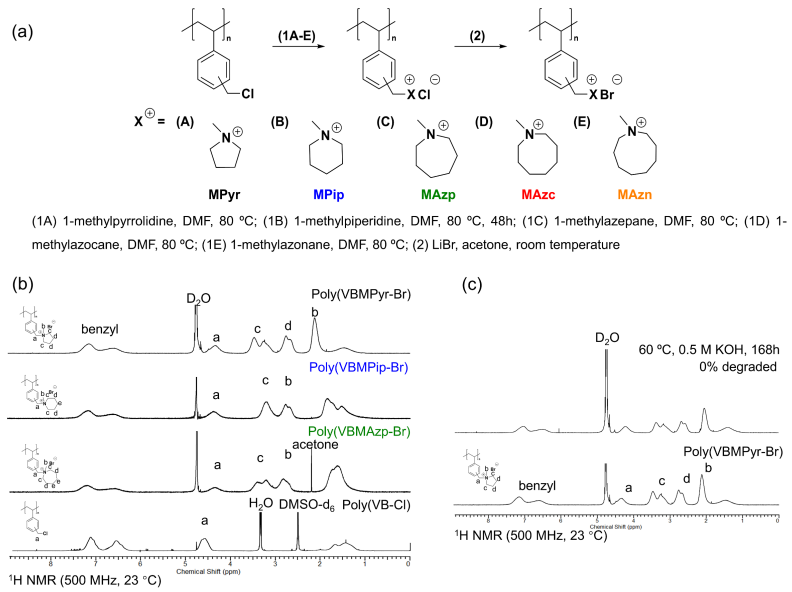
More details can be found at: Meek, K.M.; Sun, R.; Willis, C.; Elabd, Y.A. Hydroxide Conducting Polymerized Ionic Liquid Pentablock Terpolymer Anion Exchange Membranes with Methylpyrrolidinium Cations. *Polymer* **2018**, *134*, 221-226.



- Commercially Scalable
- High Hydroxide Conductivity
- Low Water Uptake
- Chemically Stable

3. Saturated *N*-Heterocyclic Cationic (SNHC) Polymers

The synthesis and exploration of new polymers bearing unique reactive and/or charged functional groups is of great interest to numerous applications (*i.e.* alkaline fuel cells and batteries). The goal of this study is to synthesize new SNHC polymers with various cation ring sizes (*e.g.*, 5-, 6-, 7-, 8-, and 9-membered rings: pyrrolidinium, piperidinium, azepanium, azocanium, azonanium, respectively) and investigate their properties for numerous applications (*i.e.* alkaline chemical stability, conductivity, *etc*.) Our preliminary results demonstrated the successful syntheses of styrene-based SNHC polymers with various cations (methylpyrrolidinium, methylpiperidinium, and methylazepanium) and bromide anion (see figure below). The chemistry and purity of the synthesized SNHC polymers were characterized with ^{1}H NMR spectroscopy, and elemental analysis (EA). ^{1}H NMR (see figure below) indicated that the SHNC polymers were fully functionalized. EA results further confirmed that the anion exchange metathesis of poly(VBMPyr-Br) was successful and highly efficient (poly(VBMPip-Br) and poly(VBAzp-Br) are in progress. Alkaline chemical stability of the styrene-based SNHC polymers with methylpyrrolidinium and methylpiperidinium cations were examined by ^{1}H NMR spectroscopy. The stability study was performed by exposing to 1 ml KOH/D_2O solution with various concentration at 60 °C for at least 168 h, followed by ^{1}H NMR experiments to quantify chemical degradation. Preliminary results showed that poly(VBMPyr-Br) exhibited 0% degradation after 168 h of exposure to 20 mol eq KOH/D_2O at 60 °C while poly(VBMPip-Cl) exhibited 0% degradation after 5 weeks of exposure to 20 mol eq KOH/D_2O at 60 °C. Future work will be focusing on the synthesis of styrene-based SNHC polymers with methylazocanium and methylazonanium cations and the alkaline chemical stability studies with various conditions on the synthesized polymers. The conductivity and water uptake of the synthesized polymers will also be examined.

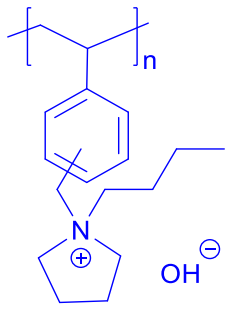


(a) Synthesis pathway of SNHC polymers. (b) ^{1}H NMR Spectra of SNHC polymers (c) ^{1}H NMR spectra for poly(VBMPyr-Br) exposed to 20 eq (0.5 M) KOH/D_2O at 60 °C for 168 h.

4. Alkaline Chemical Stability and Ion Transport in Polymerized Ionic Liquids with Various Backbones and Cations

The development of anion exchange membranes (AEMs) with high alkaline chemical stability, as well as high ion conductivity, is crucial to the implementation of long-lasting, low-cost (non-platinum) alkaline fuel cells (AFCs). In this study, twelve polymerized ionic liquids (PILs) were synthesized with various backbones and cations (backbones: ethyl methacrylate, undecyl methacrylate, undecyl acrylate, styrene; covalently attached cations: butylimidazolium, trimethylammonium, butylpyrrolidinium). ^{1}H NMR spectroscopy was employed to determine the alkaline degradation mechanisms and extent of degradation at high pH (in D_2O) at 60 °C for one week (168 h). For the butylpyrrolidinium cation, ethyl and undecyl methacrylate backbones proved to be more stable than the undecyl acrylate backbone. Styrene (vinylbenzene) functionalized with butylpyrrolidinium cation surpassed the stability of the benchmark benzyltrimethylammonium (BTMA) cation, where the former possessed the highest overall observed chemical stability with 0% degradation after one week in 20 molar equivalents KOH at 60 °C. This butylpyrrolidinium styrene-based PIL, poly(VBBP-Br), also had a high bromide conductivity of 14.5 mS cm^{-1} at 60 °C and 90% relative humidity. Additionally, poly(VBBP-Br) achieved the desirable AEM properties of relatively low water uptake (hydration number = 5.6 mol H_2O/mol cation) at high ion exchange capacity (IEC = 4.1 mmol g^{-1}). The styrene/butylpyrrolidinium pairing offers several advantages over the popular styrene/BTMA pairing (*e.g.*, higher conductivity, higher chemical stability, lower water uptake), while similarly to BTMA, allows for facile functionalization that is easily incorporated into existing AEM styrene backbones. Overall, these results show the promise and practicality of the butylpyrrolidinium styrene-based AEM chemistry for AFC applications.

More details can be found at: Meek, K.M.; Nykaza, J.R.; Elabd, Y.A. Alkaline Chemical Stability and Ion Transport in Polymerized Ionic Liquids with Various Backbones and Cations. *Macromolecules* **2016**, *49*, 3382-2294.

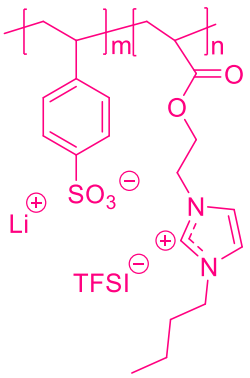


- High Alkaline Chemical Stability
- High Ionic Conductivity
- Low Water Uptake
- Facile Synthesis

5. Sulfonated Polymerized Ionic Liquid Block Copolymers

We report the successful synthesis of a new diblock copolymer referred to as sulfonated polymerized ionic liquid (PIL) block copolymer, poly(SS-Li-*b*-AEBIm-TFSI), which contains both sulfonated blocks (sulfonated styrene: SS) and PIL blocks (1-[(2-acryloyloxy)ethyl]-3-butylimidazolium: AEBIm) with both mobile cations (lithium: Li^+) and mobile anions (bis(trifluoromethylsulfonyl)imide: $TFSI^-$). Synthesis consisted of polymerization *via* reversible addition-fragmentation chain transfer, followed by post-functionalization reactions to covalently attach the imidazolium cations and sulfonic acid anions to their respective blocks, followed by ion exchange metathesis resulting in mobile Li^+ cations and mobile $TFSI^-$ anions. Solid-state films containing 1 M Li-TFSI salt dissolved in ionic liquid resulted in an ion conductivity of >1.5 mS cm^{-1} at 70 °C, where small-angle X-scattering data indicated a weakly ordered microphase-separated morphology. These results demonstrate a new ion-conducting block copolymer containing both mobile cations and mobile anions.

More details can be found at: Meek, K.M.; Elabd, Y.A. Sulfonated Polymerized Ionic Liquid Block Copolymers. *Macromolecular Rapid Comm.* **2016**, *37*, 1200-1206. *Invited Contribution, Special Issue on Ionic Liquids in Polymer Design*



Block Copolymer with
Mobile Cations and Mobile Anions

6. Polymerized Ionic Liquid Diblock Copolymer as an Ionomer and Anion Exchange Membrane for Alkaline Fuel Cells

Alkaline fuel cells have the potential to provide sustainable portable energy without high-cost platinum if robust, chemically stable anion exchange polymers can be discovered. In this study, a polymerized ionic liquid (PIL) diblock copolymer, poly(MMA-*b*-MUBIm-HCO_3), composed of an ionic liquid monomer, (1-[(2-methacryloyloxy)undecyl]-3-butylimidazolium bicarbonate) (MUBIm-HCO_3), and a non-ionic monomer, methyl methacrylate (MMA), was produced *via* anion exchange metathesis from the precursor bromide conducting PIL block copolymer, poly(MMA-*b*-MUBIm-Br), at two PIL compositions (20.0 and 37.9 mol%). Prior to anion exchange, the precursor block copolymer was synthesized *via* the reverse addition fragmentation chain transfer (RAFT) polymerization technique. Non-porous, dense membranes fabricated from this PIL block copolymer were highly conductive, transparent, flexible, and water insoluble. Membrane electrode assemblies were fabricated with this polymer as both the solid-state membrane separator and the ionomer in the catalyst layers using three different techniques: Painted Gas Diffusion Layer (GDL), Air Spray GDL, and Decal Transfer. Alkaline fuel cell (AFC) performance was measured as a function of fuel cell operating conditions, MEA fabrication technique, membrane thickness, and ionomer in different anion exchanged forms. AFC maximum power density of approximately 30 mW cm^{-1} was obtained for H_2/O_2 fuel, 25 psig (172 kPa) back pressure, 50 μm thick membrane using the Painted GDL MEA fabrication technique. For the first time, these results demonstrate the feasibility of using PIL block copolymers as the membrane and ionomer in alkaline fuel cells.

More details can be found at: Nykaza, J.R.; Benjamin, R.; Meek, K.M. Elabd, Y.A. Polymerized Ionic Liquid Diblock Copolymer as an Ionomer and Anion Exchange Membrane for Alkaline Fuel Cells. *Chemical Engineering Science* **2016**, *154*, 119-127. *Invited Contribution, Special Issue on Recent Advances in Energy Conversion and Storage Devices*

7. Transport-Morphology Relationships in PIL Bock Copolymers

Transport-morphology relationships in polymerized ionic liquid (PIL) block copolymers were explored as a function ionic concentration or PIL composition. Both bromide and hydroxide

conductivities were higher in the PIL block copolymer at PIL compositions of 11.9, 17.3, and 26.5 mol% compared to the PIL homopolymer under the same experimental conditions, even though the homopolymer possessed a higher water and ionic content compared to the block copolymers. These unusual results suggest that the confinement of the PIL microdomain within the block copolymer morphology enhances ion transport compared to its predicted value.

More details can be found at: Meek, K.M.; Sharick, S.; Ye, Y.; Winey, K.I.; Elabd, Y.A. Bromide and Hydroxide Conductivity-Morphology Relationships in Polymerized Ionic Liquid Block Copolymers. *Macromolecules* **2015**, *48*, 4850-4862.

8. Water/Ion Clustering in PIL Bock Copolymers

Transport-morphology relationships in PIL block copolymers were explored as a function of morphology type by examining two polymerized ionic liquid (PIL) diblock copolymers with similar chemistries but different side alkyl spacer chain lengths (ethyl versus undecyl). When saturated in liquid water, water/ion clusters were observed only in the PIL block copolymer with longer alkyl side chains (undecyl) as evidenced by both small-angle neutron scattering and intermediate-angle X-ray scattering, i.e., water/ion clusters form within the PIL microdomain under these conditions. The resulting bromide ion conductivity in the undecyl sample was higher than the ethyl sample (14.0 mS cm^{-1} versus 6.1 mS cm^{-1} at 50 °C in liquid water) even though both samples had the same block copolymer morphology (lamellar) and the undecyl sample had a lower ion exchange capacity (0.9 meq g^{-1} versus 1.4 meq g^{-1}) (see figure below). These results show that small chemical changes to ion-containing block copolymers can induce water/ion clusters within block copolymer microdomains and this can subsequently have a significant effect on ion transport.

More details can be found at: Nykaza, J.R.; Ye, Y.; Nelson, R.L.; Jackson, A.C.; Beyer, F.L.; Davis, E.M.; Page, K.A. Sharick, S.; Winey, K.I.; Elabd, Y.A**.** Polymerized Ionic Liquid Diblock Copolymers: Impact of Water/Ion Clustering on Ion Conductivity. *Soft Matter* **2016**, *12*, 1133-1144.

9. Alkaline Chemical Stability in PILs with Different Cations

The alkaline chemical stability of hydroxide conducting PILs with various cations was investigated. The degradation mechanisms and extent of degradation was quantified using ^{1}H NMR spectroscopy at various pHs (in D_2O), temperatures, and times. The PILs with imidazolium and pyrrolidinium cations showed enhanced chemical stability relative to the PILs with ammonium and phosphonium cations.

More details can be found at: Meek, K.M.; Elabd, Y.A. Alkaline Chemical Stability of Polymerized Ionic Liquids with Different Cations. *Macromolecules* **2015**, *48*, 7071-7084.

Training Opportunities:

Students trained include:

Rishon Benjamin – received his B.S. from Drexel University, June 2015. He is currently a graduate student at M.I.T.

Kelly M. Meek – received her Ph.D. from Texas A&M University, May 2016. She is currently postdoc at Oak Ridge National Laboratory (ORNL). She will be seeking future faculty position.

Dissertation: **Meek, K.M.** Ph.D. Dissertation, Alkaline Chemical Stability and Ion Transport in Polymerized Ionic Liquid Anion Exchange Membranes, Texas A&M University, May 2016.

Jacob R. Nykaza – received his Ph.D. from Drexel University, April 2016. He is currently employed at Teledyne Technologies

Dissertation: **Nykaza, J.R.** Ph.D. Dissertation, Imidazolium-Based Block Copolymers as Solid-State Separators for Alkaline Fuel Cells and Lithium Ion Batteries, Drexel University, April 2016.

Rui Sun – received her M.S. from Texas A&M University, August 2016. She is now a Ph.D. student at Texas A&M University and working on this project.

Thesis: **Sun, R.** M.S. Thesis, Polymerized Ionic Liquid Derived Carbon, Texas A&M University, August 2016.

Patrick Lathrop – is currently a Ph.D. student at Texas A&M University and is working on this project.

Results Dissemination:

Key Peer-Reviewed Publications:

1. Meek, K.M.; Sun, R.; Willis, C.; Elabd, Y.A. Hydroxide Conducting Polymerized Ionic Liquid Pentablock Terpolymer Anion Exchange Membranes with Methylpyrrolidinium Cations. *Polymer* **2018**, *134*, 221-226.

2. Nykaza, J.R.; Li, Y.; Elabd, Y.A.; Snyder, J.D. Effect of Alkaline Exchange Polymerized Block Copolymer Ionomers on the Kinetics of Fuel Cell Half Reactions. *J. Electroanalytical Chem.* **2016**, *783*, 182-187.

3. Nykaza, J.R.; Savage, A.M.; Pan, Q.; Wang, S.; Beyer, F.L.; Tang, M.H.; Li, C.Y.; Elabd, Y.A. Polymerized Ionic Liquid Diblock Copolymer as Solid-State Separator and Electrolyte in Lithium-Ion Battery. *Polymer* **2016**, *101*, 311-318.

4. Nykaza, J.R.; Benjamin, R.; Meek, K.M. Elabd, Y.A. Polymerized Ionic Liquid Diblock Copolymer as an Ionomer and Anion Exchange Membrane for Alkaline Fuel Cells. *Chemical Engineering Science* **2016**, *154*, 119-127. *Invited Contribution, Special Issue on Recent Advances in Energy Conversion and Storage Devices*

5. Meek, K.M.; Elabd, Y.A. Sulfonated Polymerized Ionic Liquid Block Copolymers. *Macromolecular Rapid Comm.* **2016**, *37*, 1200-1206. *Invited Contribution, Special Issue on Ionic Liquids in Polymer Design*

6. Meek, K.M.; Nykaza, J.R.; Elabd, Y.A. Alkaline Chemical Stability and Ion Transport in Polymerized Ionic Liquids with Various Backbones and Cations. *Macromolecules* **2016**, *49*, 3382-2294.

7. Nykaza, J.R.; Ye, Y.; Nelson, R.L.; Jackson, A.C.; Beyer, F.L.; Davis, E.M.; Page, K.A. Sharick, S.; Winey, K.I.; Elabd, Y.A**.** Polymerized Ionic Liquid Diblock Copolymers: Impact of Water/Ion Clustering on Ion Conductivity. *Soft Matter* **2016**, *12*, 1133-1144.

8. Meek, K.M.; Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers for Electrochemical Energy. *Journal of Materials Chemistry A* **2015**, *3*, 24187-24194. *Invited Contribution*

9. Meek, K.M.; Elabd, Y.A. Alkaline Chemical Stability of Polymerized Ionic Liquids with Different Cations. *Macromolecules* **2015**, *48*, 7071-7084.

10. Ansaloni, L.; Nykaza, J.R.; Ye, Y.; Elabd, Y.A.; Giacinti Baschetti, M. Influence of Water Vapor on the Gas Permeability of Polymerized Ionic Liquid Membranes. *J. Membr. Sci.*, **2015**, *487*, 199-208.

11. Meek, K.M.; Sharick, S.; Ye, Y.; Winey, K.I.; Elabd, Y.A. Bromide and Hydroxide Conductivity-Morphology Relationships in Polymerized Ionic Liquid Block Copolymers. *Macromolecules* **2015**, *48*, 4850-4862.

12. Nykaza, J.R.; Ye, Y.; Elabd, Y.A. Polymerized Ionic Liquid Diblock Copolymers with Long Alkyl Side-Chain Length. *Polymer* **2014**, *55*, 3360-3369. *Invited Contribution, Special Issue on Polymerized Ionic Liquids*

Key Presentations:

Oral Presentations:

1. Sun, R.; Meek, K.M.; Elabd, Y.A. Carbon Derived from Polymerized Ionic Liquids. AIChE Annual Meeting, Minneapolis, MN, November 2017.

2. Meek, K.M.; Nykaza, J., Sun, R.; Willis, C.L.; Elabd, Y.A. Chemical Stability and Ion Transport in Polymerized Ionic Liquid Anion Exchange Membranes. Fall National Meeting of the American Chemical Society, Washington, D.C., August 2017. **Selected as DSM Science & Technology Award Finalist**

3. Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers for Alkaline Fuel Cells. Materials Research Society Fall National Meeting, Boston, MA, November 2016. **Invited Speaker**

4. Meek, K.M.; Nykaza, J., Sun, R.; Willis, C.L.; Elabd, Y.A. Chemical Stability and Ion Transport in Polymerized Ionic Liquid Anion Exchange Membranes. AIChE Annual Meeting, San Francisco, CA, November 2016. **Selected for Excellence in Graduate Polymer Research Session – Received 2nd Place Award in Session**

5. Santos, M.; Elabd, Y.A. *In Situ* Pressure-Contact Time-Resolved Fourier Transform Infrared Attenuated Total Reflectance Spectroscopy: A New Method to Measure Liquid Diffusion in Free-Standing Polymer Films. AIChE Annual Meeting, San Francisco, CA, November 2016. AIChE, San Francisco, CA, November 2016.

6. Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers for Alkaline Fuel Cells. American Chemical Society Southwest Regional Meeting (ACS-SWRM), Galveston, TX, November 2016. **Invited Speaker**

7. Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers. American Chemical Society Meeting on Advanced Polymer Materials (ACS-APM), Houston, TX, November 2016. **Invited Speaker**

8. Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers for Alkaline Fuel Cells. 15th International Symposium on Polymer Electrolytes. Uppsala, Sweden, August 2016. **Invited Speaker**

9. Elabd, Y.A. Membranes for Fuel Cells. European Membrane Society Summer School, Bertinoro, Italy, June 2016. **Invited Speaker**

10. Meek, K.M.; Savage, A.M.; Beyer, F.L.; Elabd, Y.A. Chemical Stability and Ion Transport in Polymerized Ionic Liquid Block Copolymer Anion Exchange Membranes with Various Cations. AIChE Annual Meeting, Salt Lake City, UT, November 2015.

11. Nykaza, J.R.; Li, Y.; Elabd, Y.A.; Snyder, J. The Hydroxide Conductivity and Chemical Stability of a Polymerized Ionic Liquid Diblock Copolymer for Alkaline Fuel Cells Using Rotating Disk Electrode. AIChE Annual Meeting, Salt Lake City, UT, November 2015.

12. Elabd, Y.A. Polymerized Ionic Liquid Block Copolymer as Anion Exchange Membranes. Fall National Meeting of the American Chemical Society, Boston, MA, August 2015. **Invited Speaker**

13. Meek, K.M.; Beyer, F.L.; Elabd, Y.A. Transport and Morphology of Polymerized Ionic Liquid Block Copolymer Anion Exchange Membranes with Various Cations. Spring National Meeting of the American Chemical Society, Denver, CO, March 2015.

14. Nykaza, J.R.; Sharick, S.; Davis, E.M.; Ye, Y.; Page, K.A.; Jackson, A.; Beyer, F.L.; Winey, K.I.; Elabd, Y.A. Impact of Alkyl Chain Length on Ion Conduction and Morphology in Polymerized Ionic Liquid Diblock Copolymers. Spring National Meeting of the American Chemical Society, Denver, CO, March 2015.

15. Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers: Highly Versatile Ion Conductors. Annual Meeting of the American Institute of Chemical Engineers, Atlanta, GA, November 2014. **Invited Speaker**

16. Ye, Y.; Nykaza, J.R.; Meek, K.M.; Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers as Anion Exchange Membranes for Alkaline Fuel Cells. Annual Meeting of the American Institute of Chemical Engineers, Atlanta, GA, November 2014. **Invited Speaker**

17. Ansaloni, L.; Nykaza, J.R.; Minelli, M.; Elabd, Y.A.; Giaciniti Baschetti, M. Polymerized Ionic Liquid Membranes for CO_2 Capture: The Effect of Water Vapor. Annual Meeting of the American Institute of Chemical Engineers, Atlanta, GA, November 2014.

Poster Presentations:

18. Sun, R.; Meek, K.M.; Elabd, Y.A. PIL-Derived Carbon. AIChE Annual Meeting, San Francisco, CA, November 2016.

19. Lathrop, P.; Elabd, Y.A. Polymerized Ionic Liquid Triblock Terpolymers: Synthesis and Characterization. AIChE Annual Meeting, San Francisco, CA, November 2016.

20. Benjamin, R.; Nykaza, J.R.; Elabd, Y.A. Alkaline Fuel Cell Performance with a Polymerized Ionic Liquid Block Copolymer as Anion Exchange Membrane. Annual Meeting of the American Institute of Chemical Engineers, Atlanta, GA, November 2014. **Received 3rd Place Award in the Materials Science and Engineering Poster Competition**

21. Nykaza, J.R.; Elabd, Y.A. Polymerized Ionic Liquid Block Copolymers as Solid-State Polymer Electrolytes for Lithium-Ion Batteries. Annual Meeting of the American Institute of Chemical Engineers, Atlanta, GA, November 2014.

Honors:

Prof. Elabd was elected as an APS Fellow

Prof. Elabd was named the Joe M. Nesbitt Professor

Kelly Meek received 2017 DSM Science & Technology Award Finalist (@Fall 2017 ACS National Meeting)

Kelly Meek received 2nd Place Award in Excellence in Graduate Polymer Research Session (@2016 AIChE National Meeting)

Kelly Meek received the 2015 Phillips 66 Fellowship (awarded to top PhD student in Chemical Engineering Department at Texas A&M University)

Collaboration:

Two co-authored publications with Dr. Rick Beyer (ARL-WMRD).

Nykaza, J.R.; Savage, A.M.; Pan, Q.; Wang, S.; Beyer, F.L.; Tang, M.H.; Li, C.Y.; Elabd, Y.A. Polymerized Ionic Liquid Diblock Copolymer as Solid-State Separator and Electrolyte in Lithium-Ion Battery. *Polymer* **2016**, *101*, 311-318.

Nykaza, J.R.; Ye, Y.; Nelson, R.L.; Jackson, A.C.; Beyer, F.L.; Davis, E.M.; Page, K.A. Sharick, S.; Winey, K.I.; Elabd, Y.A**.** Polymerized Ionic Liquid Diblock Copolymers: Impact of Water/Ion Clustering on Ion Conductivity. *Soft Matter* **2016**, *12*, 1133-1144.

Technology Transfer:

Collaboration with industry – Kraton Polymers – one co-authored publication.

Meek, K.M.; Sun, R.; Willis, C.; Elabd, Y.A. Hydroxide Conducting Polymerized Ionic Liquid Pentablock Terpolymer Anion Exchange Membranes with Methylpyrrolidinium Cations. *Polymer* **2018**, *134*, 221-226.